

RELAXATION OF Cu(100), (110) AND (111) SURFACES USING *AB INITIO* PSEUDOPOTENTIALS

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The geometries of the Cu(100), Cu(110) and Cu(111) surfaces are determined using *ab initio* pseudopotential calculations. Use of the Hellmann–Feynman theorem to calculate forces allows the determination of the equilibrium atomic positions with a small number of trial geometries. Our calculated results show that the surface relaxation of Cu(100) and Cu(110) surfaces are inward relaxations, while that of Cu(111) surface is slightly outward relaxation. Our results show that the forces, charge transfer and the detailed electronic structure of the Cu surface will affect the relaxation of the outermost layer. The calculated results are in good agreement with the results obtained by various experiments.

1. Introduction

The determination of the structure of surfaces is a basic question in surface science. Atoms near the surface of a crystal are under the influence of different forces from those in the bulk. This leads in most cases to relaxations or reconstructions.¹ Such changes in geometry can have significant effects on the physical properties of the metal surface (e.g. changes in work functions, reactivities, etc.).² This topic has therefore received much attention in the past two decades.

Many theoretical calculations and experimental measurements have been performed on surface stress and surface relaxation of fcc metals.^{1–18} The simplest level involves pair-potential calculations (e.g. L–J potentials), which are too unrealistic to be of use for quantitative, and sometimes even qualitative, predictions.⁷ The intermediates in terms of complexity and computational cost are several semiempirical methods such as effective-crystal theory (ECT),⁹ effective medium theory (EMT)¹⁹ and embedded atom methods (EAM)^{8,10} and so on. The surface relaxations calculated from such semiempirical methods are not reliable enough, especially

for some “anomalous” surfaces, e.g. Al(100),^{17,20} Al(111),^{7,21} Pt(111)^{22,23} and Cu(111).¹⁴ The relaxations of the above “anomalous” surfaces are predicted to be inward relaxation from many semiempirical methods, while the experimental measurements show outward relaxation. The most accurate and state-of-the-art methods are first principle calculations. Such methods are more complicated and computationally costly but more accurate for surface relaxation and surface stress calculations using first principle methods compared to pair-potential or semiempirical methods. To calculate surface geometries, two main approaches have been suggested, i.e. the cluster approach and the slab or slab-superlattice approach. It is well known that the slab approach is generally better than the cluster approach since it keeps the symmetries within the plane of the slab, which is close to the real surface.²⁴

First principle total-energy calculations have been very successful in determining the structural properties of a large variety of bulk materials.²⁵ However, application to surfaces has become feasible only recently due to the rapid development of high performance computers. A number of clean metal

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surfaces as well as adsorbate systems have been studied by first principle total-energy calculations and calculated relaxations agree generally very well with the observed structures.²⁶

The geometries of some well-studied surfaces still remain uncertain or under further investigation. For example, for the Al(100) surface, many semiempirical methods such as EAM,²⁷ ECT²⁸ and EMT,²⁹ as well as surface-embedded Green's function theory (SEGF),³⁰ predicted an inward relaxation, which is in contradiction with experimental measurements. Previous pseudopotential, modified embedded atom method (MEAM)⁷ and our recent pseudopotential studies¹⁷ all show the outward relaxation for the Al(100) surface. The results agree quite well with experiments and the physical picture for the underlying driving mechanism was elucidated. Apart from the simple metal Al, there is still some disagreement about the relaxation of the transition metal Cu, in particular the Cu(111) surface.⁷ Previous experimental measurements show that Cu(111) displays small inward relaxation; $-0.3 \pm 1.0\%$ in Ref. 15 and $-0.7 \pm 0.5\%$ in Ref. 16. Previous semiempirical methods⁸⁻¹⁰ and first principle calculations¹ predicted inward relaxation. However, the latest VLEED experiment¹⁴ showed an outward relaxation of the Cu(111) surface.

To investigate the relaxation behavior of transition low index surfaces and the underlying physical picture, *ab initio* pseudopotential calculations with mixed-basis representation have been performed in this study. As an example, we study the multilayer relaxation of the low index surfaces of Cu.

To understand the physical basis behind the surface relaxation, forces on atomic layers and charge density are compared for Cu(100), Cu(110) and

Cu(111) surfaces and their relations to relaxation behaviors are also discussed.

2. Method of Calculation

The total-energy calculations of Cu(100) and (110) surfaces are performed using the plane wave *ab initio* pseudopotential method within the local density functional (LDF) theory. Nonlocal norm-conserving pseudopotentials are created according to the prescription of Hamann *et al.*³¹ The Hedin-Lundqvist³² form of the exchange-correlation potential and a mixed basis representation are employed. The wave functions are expanded into plane waves up to a cutoff energy of 14.5 Ry. Considering the fairly sharp local orbitals of transition metals, we supplement the plane wave basis with local orbitals centered on the atomic sites, which is the so-called "mixed-basis technique."¹⁸ This technique was originally introduced by Louie, Ho and Cohen³³ to calculate the electronic structures of transition metals, and subsequently extended to include total energy and force calculations.³⁴⁻³⁷ Usually just a few local orbitals per atom are needed, and when they are optimized carefully, most elements can be converged reasonably well with a plane wave cutoff of about 10 Ry.¹⁸ This approach has been applied successfully to the electronic, structural and lattice dynamical properties of a large variety of transition metal systems.¹

The k integration over the Brillouin zone is performed on a $4 \times 4 \times 1$ Monkhorst-Pack mesh. Our total-energy calculations are based on slab geometry in which multiple surfaces are presented. The top view of the Cu(100), Cu(110) and Cu(111) surfaces are showed in Fig. 1. The supercell contains

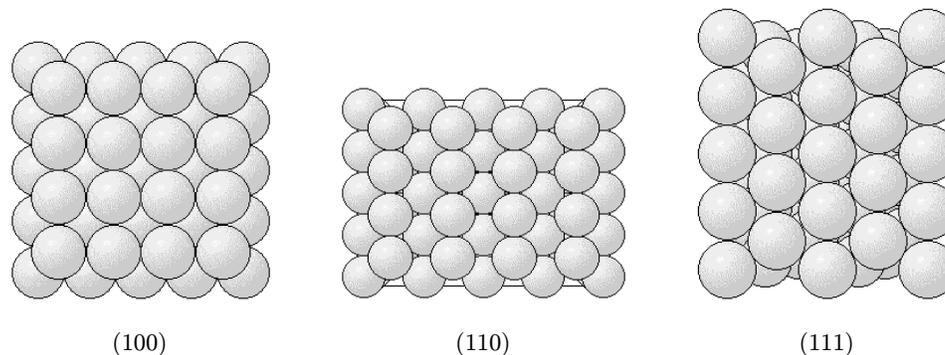


Fig. 1. Top view of the (100), (110) and (111) surfaces of Cu.

nine layers of Cu and a vacuum layer of thickness ~ 8.5 Å. The slabs are fully relaxed by the Hellmann–Feynman (H–F) force method and the criterion is for the H–F force to be less than 0.5×10^{-3} Ry/au.

3. Results

Before performing the surface calculations, we calculate the total energy as a function of the lattice constant for bulk Cu (fcc) metal carefully. We determine the equilibrium lattice constant as 3.592 Å, which is consistent with experimental data, 3.60 Å. We then perform the slab calculations using the equilibrium lattice constant to investigate the surface relaxation of low index Cu surfaces.

The multilayer relaxation of Cu(100), (110) and (111) surfaces calculated by *ab initio* pseudopotentials with mixed-basis representation are listed in Tables 1, 2 and 3 respectively. We first discuss the multilayer relaxation of the Cu(100) surface. The experimental data (as shown in Table 1) show that the surface relaxation of Cu(100) is slightly inward, ranging from -1.1% to -2.1% . Our calculations give -1.06% for the topmost layer relaxation, which agrees with measurements quite well. Previous semiempirical methods and first principle calculation predicted the same trends but with slightly larger

relaxation. Recent MEAM calculation gave a smaller relaxation of -0.83% .

For the Cu(110) surface, the relaxation is normal inward relaxation and the magnitude is large compared to the Cu(100) surface. Our pseudopotential results give -7.76% relaxation for Cu(110), in agreement with experimental data, which ranges from -5.3% to -10.0% , as well as other theoretical results. The second layer relaxation is an expansion with a magnitude of 4.17% in this work, which is slightly larger than that of experimental data but consistent with that by MEAM (4.41%).

The Cu(111) surface is the most closely packed surface. Its multilayer relaxation is quite small. In contrast to the Cu(100) and Cu(110) surfaces, Cu(111) exhibits “anomalous” outward relaxation in this work, i.e. $+0.56\%$. Previous experiments suggested an inward relaxation ranging from -0.3% to -0.7% , while the latest LEED experimental results give a small expansion ($0.5\text{--}1\%$). For the theoretical calculations, ECT, EAM and first principle calculations all predicted an inward relaxation. While recent theoretical calculations by MEAM predicted a small outward relaxation (0.14%), our results agree quite well with the latest LEED experiment and MEAM calculations.

Table 1. Comparison of experimental and theoretical surface structure of Cu(100).

Theory or experiment	Relaxation (%)				Method	Reference No.
	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}		
Present study	-1.06	-0.65	1.28	-0.58	<i>ab initio</i> pseudopotential	
Experiment	-1.1 ± 0.4	1.70 ± 0.6				3
	-1.1 ± 0.4	2.0 ± 0.8				3
	-1.2	0.9				4
	-2.1	0.45				5
	-1.1	1.7				6
Theory	-0.83	0.04	-0.00	0.00	MEAM	7
	-3.79	-0.54	0.02	0.00	EAM	8
	-3.7	0.7			ECT	9
	-1.4	-0.3			EAM	10
	-3.0	0.1	-0.2		FP	1

Table 2. Comparison of experimental and theoretical surface structure of Cu(110).

Theory or experiment	Relaxation (%)				Method	Reference No.
	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}		
Present study	-7.76	4.17	3.70	-0.47	<i>ab initio</i> pseudopotential	
Experiment	-7.9	2.4				3
	-10.0	1.9				3
	-8.5	2.3				11
	-5.3 ± 2.4	3.3 ± 1.5				11
	-8.5 ± 0.6	2.3 ± 0.8				12
	-10.0 ± 2.5	0.0 ± 2.5				13
Theory	-8.93	4.41	-1.92	1.10	MEAM	7
	-8.73	1.56	-1.20	0.43	EAM	8
	-6.3	0.2			ECT	9
	-4.9	0.23			EAM	10
	-9.3	2.8	-1.1		FP	1

Table 3. Comparison of experimental and theoretical surface structure of Cu(111).

Theory or experiment	Relaxation (%)				Method	Reference No.
	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}		
Present study	0.56	-0.07	0.55	0.20	<i>ab initio</i> pseudopotential	
Experiment	0.5 ~ 1				VLEED	14
	-0.3 ± 1.0					15
	-0.7 ± 0.5					16
Theory	0.14	-0.01	0.00	0.00	MEAM	7
	-2.48	-0.04	0.00	0.00	EAM	8
	-3.1	1.6			ECT	9
	-1.4	-0.04			EAM	10
	-1.3	0.6	-0.3		FP	1

4. Discussion

For fcc metal surfaces, there have been several models proposed for surface relaxations.^{7,38} We describe three main models for inward relaxation, as follows:

- (i) When a crystal is cut to form a surface, the electronic charge density relaxes so as to weaken its corrugation. The smoothing of the electron charge density reduces its kinetic energy

and results in the shift of electrons toward the surface. This attracts the positive ion cores closer to the rest of the crystal.

- (ii) Based on effective-medium theory (EMT) of metallic bonding, when a crystal is truncated to form a surface, the surface atoms that have lost electron density tend to move in such a way as to return to the optimal electron density and thus move toward the rest of crystal.

(iii) The third explanation for topmost-layer contraction is that it is a natural consequence of the bond-order-bond-length correlation. Here the operative principle is saturation of valence. Every atom has a fixed number of valence electrons. If a surface is formed, the surface atoms lose several neighbors. The electrons that are involved in bonding to these neighbors therefore redistribute themselves nearer (i.e. “back-bonding”) to the atoms in the layer below. This strengthens the bond between the first and second atomic layers, thus leading to an inward relaxation.

In this study, Cu(100) and Cu(110) show normal inward relaxation, while Cu(111) shows “anomalous”

outward relaxation. A direct method of understanding fcc metal surface relaxation is to check the interplanar forces of the unrelaxed geometry. The results are shown in Table 4. The sign of the forces on the topmost layer of Cu(100) and (110) for the unrelaxed geometry is negative but that

Table 4. Calculated forces on the topmost layer in the unrelaxed geometry. Positive value indicates direction of force is towards the surface. Negative value indicates force is directed into the bulk.

Force (mRy/a.u.)		
(100) unrelaxed	(110) unrelaxed	(111) unrelaxed
-53.4	-9.3	46.9

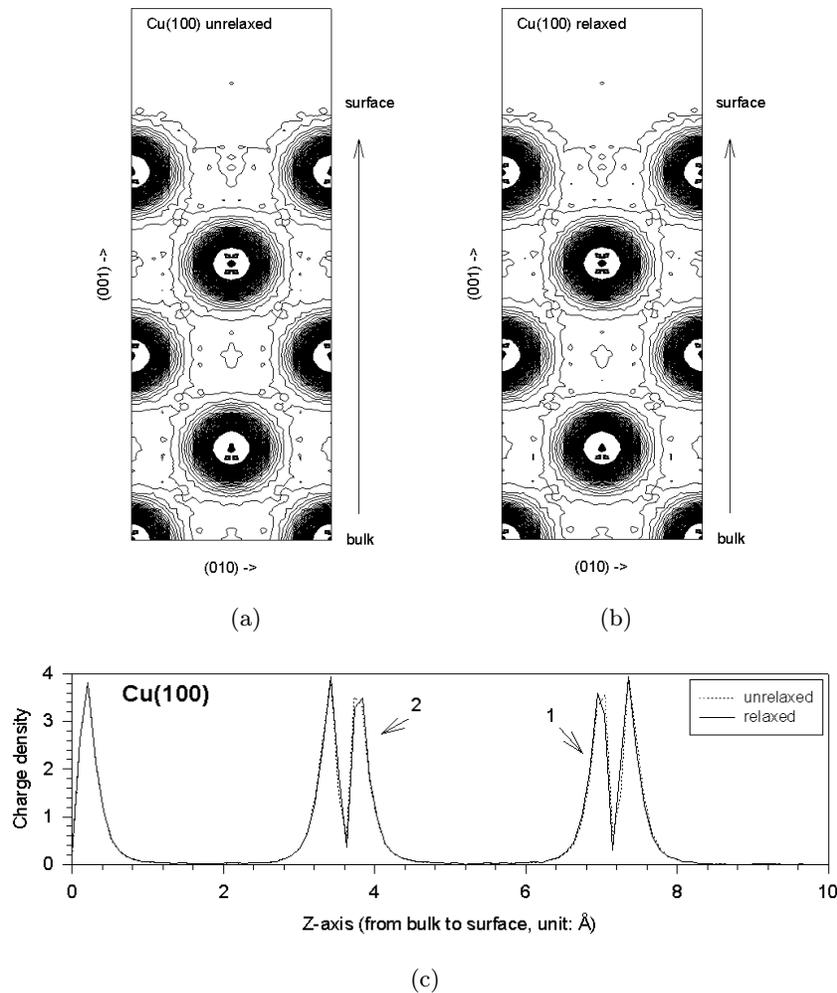


Fig. 2. Charge density of the Cu(100) slab along the z axis (from bulk layers to the vacuum region) without (a) and with (b) relaxations. The comparisons between the charge density for slab without and with relaxation along the edge of Figs. (a) and (b) are shown in Fig. (c).

on Cu(111) is positive. The sign of forces correlate quite well with the final relaxations. One will note that the force on the topmost layer of the (110) surface is smaller than that of (100) and (111), but the relaxation is the largest. This is because the forces on the second layer for (110) are much larger than that for (100) and (111), and the multilayer relaxations affect the final relaxation of the topmost layer.

Besides force analysis, an analysis of the electron density of Cu slabs will help us to understand the expansion or contraction at the surface. We show the charge density of the Cu(100) slab with and without relaxation in Fig. 2. The charge density of the topmost layer decreases slightly and that of the second layer increases slightly. Moreover, the charge density of the topmost layer shifts a little into the bulk. A similar result occurs for Cu(110) but the result is reversed for Cu(111). Such information indicates that the Cu(100) and Cu(110) surface may form “back-bonding,” which is related to inward relaxations; while Cu(111) does not form “back-bonding” and therefore displays outward relaxation instead.

From the viewpoint of electronic structure, the outward relaxation may be induced by the “details” of surface electronic structure as discussed in many first principle calculations. For example, the outward relaxation of the Pd(100) surface is due to the nearly filled d band.³⁹ In this study, we observe that the

surface electronic structure affects the relaxation behavior. The density of states (DOS) of Cu(110) and Cu(111) with and without relaxation are shown in Fig. 3. The DOS of the d band for the topmost layer in Cu(111) becomes narrower when the outermost atoms are moved outward. This behavior of the DOS for the outermost layer has been presumed to drive the anomalous outward relaxation, as indicated in Ref. 39. For Cu(110), the DOS becomes wider or shows almost no change after relaxation. A similar phenomenon is also observed for Cu(100). The different DOS behavior of Cu(100) and Cu(111) therefore leads to inward relaxation.

5. Conclusion

In conclusion, an *ab initio* pseudopotential with mixed basis has been used to investigate the multilayer relaxation of low index Cu surfaces. The close-packed surfaces such as (100) and (111) show smaller relaxations while the open (110) surface shows larger relaxation. Our results show that the surface relaxations of Cu(100) and (110) surfaces are inward relaxations, with magnitudes of -1.06% and -7.76% respectively, agreeing well with experimental measurements. For the Cu(111) surface, we predict an outward relaxation, which contrasts with many semiempirical theories and previous

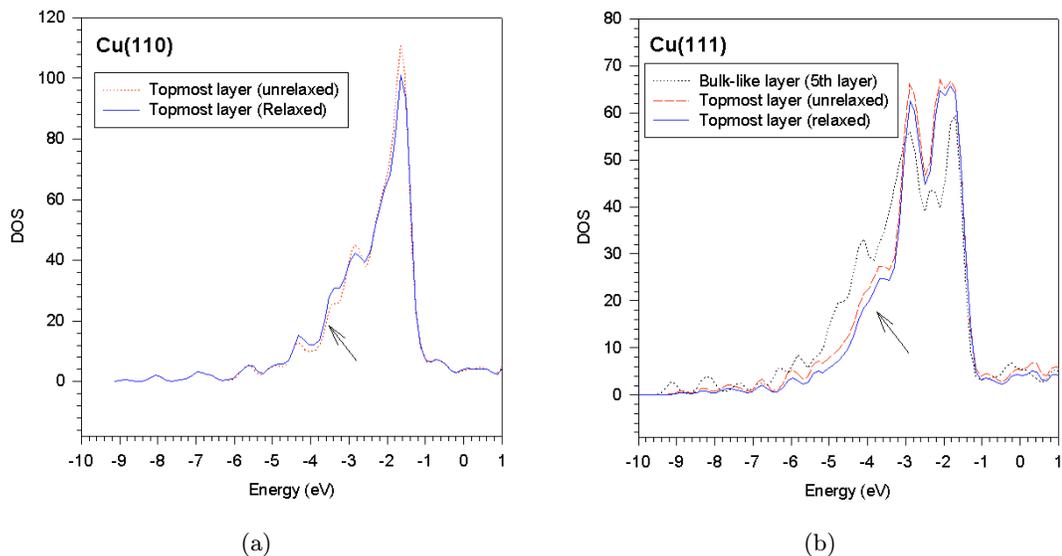


Fig. 3. Density of states (DOS) of the topmost layer in Cu(110) (a) and Cu(111) (b) slabs, with and without relaxation. The DOS of the bulklike layer (fifth layer) of the Cu(111) slab is also shown in (b).

experiments but is consistent with the latest experimental data and recent MEAM calculations. The relaxation behavior of low index Cu surfaces is directly related to Hellmann–Feynman (H–F) forces on atomic layers and change to the charge density in the surface region. For the unrelaxed surface (ideal lattice), if the force on the topmost layer is directed from bulk to surface, the relaxation will be outward. Otherwise, it is inward. As for the charge density in the surface region, for inward relaxation, the charge will transfer from surface to bulk (or sublayer), forming the so-called “back-bonding.” For outward relaxation, the charge will transfer from the surface layer (or sublayer) to vacuum without back-bonding. The detailed electronic structure of the Cu surface affects the relaxation of the outmost layer. For Cu(111), the narrower d band DOS drives the anomalous outward relaxation, while for Cu(100) and Cu(110), the d band DOS are wider or almost unchanged after relaxation.

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